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Structural and Dielectric Properties of $(Bi_2O_3Fe_2O_3)_{0.4}(Nb_2O_5)_{0.6}$ for Different Sintering Temperature

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Abstract

In this research work, $(Bi_2O_3Fe_2O_3)_{0.4}(Nb_2O_5)_{0.6}$ was made by the solid state reaction method. Samples were sintered at four different temperatures (850˚C, 925˚C, 1000˚C and 1150˚C) to study the effect of sintering temperature on the various properties of the samples. X-ray diffraction analysis confirmed that single phase $Bi_{1.721}\delta_{0.089}Fe_{1.056}Nb_{1.134}O_7$ was found when sintering temperature increased. At the same time, larger grain size was found when sintering temperature increased. From variation of dielectric loss with respect to frequency, a small peak was found when sample was sintered at higher temperature (1150˚C). Dielectric constant of the sample decreases with the increase of frequency for all the samples. With the variation of temperature, DC resistivity of the samples showed that resistivity decreases with the increase of measuring temperature which indicates semiconducting nature.

Keywords

XRD, Niobium, SEM, Dielectric Constant, Dielectric Loss, Loss Tangent, Bismuth Ferrite, Resistivity

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1. Introduction

A switchable and well-off electrical polarization is performed by a ferroelectric crystal in which constituent atomic translocation is also evolved. Similarly a static and switchable magnetization is manifested by ferromagneticcrystal which spreads due to alteration in quantum mechanical phenomenon. Materials in which two of the explained properties displayed are familiar as Multiferroic [1]. At present, bismuth ferrite (BFO) is a very well-known multiferroic. Present interest on bismuth ferrite is inspired by a paper of Ramesh's group which was published in 2003. From their research, it can be said that BFO displays large Remnant polarization with extremely large ferromagnetism [2]. The room temperature phase of $BiFeO_3$ is rhombohedral with perovskite structure [3]. Finding the saturated magnetic loops for BFO is difficult because of its weak antiferromagnetic nature. Its ferroelectric properties are impeded by enormous leakage current and low-lying resistivity. According to Hill [4], generation of net magnetization in Bismuth Ferrite begins from Fe atoms, where the net polarization of Bismuth Ferrite begins from Bi atoms. For suppressing the leakage currents of bismuth ferrite, various doping techniques have been proposed. At present, it has been proved that for increasing resistivity, and to rectify the overall properties of BFO, co-substitutions of Bi^{3+} by Nd^{3+} and partial substitution of Fe^{3+} by high valence V^{5+} and Mn^{4+} Ti^{4+} are necessary. Increasing electrical resistivity as well as decreasing charged effects can be obtained by partial substitution of Fe^{3+} by Nb^{5+} [3]. In previous research work, Dielectric, Magnetic and Magneto-electric properties of BFO were exhibited, where Nb was used as co-doping material. Moreover, piezoresponse behavior of BFO was observed, when doping had been done by Nb. From other work, we have seen that Nd doped bismuth ferrite has capacity to minimize leakage current. But in our research work, we will perform Structural, Dielectric and DC Electrical properties of BFO by doping it with only Nb.

2. Experimental Work

2.1. Preparation of Samples

$(Bi_2O_3Fe_2O_3)_{0.4}(Nb_2O_5)_{0.6}$ was manufactured by employing solid state ceramic routing. For the preparation of the samples, 99.9% pure (Aldrich, India) Bi_2O_3, 99.9% pure (LobaCheme, India) Fe_2O_3, 99.9% pure (Merck, Germany) Nb_2O_5 were used as raw materials. Required amount of high purity Bi_2O_3 and Fe_2O_3 were weighed cautiously and mixed completely in an agate mortar for 1 hour. Mixed oxide was again thoroughly mixed using stabilized ZrO_2 balls in ethanol. After 24 hour milling in ethanol medium the solution was dried at 100˚C for 24 hour. Dried samples were again pasted with binder (Polyvinyl Alcohol, 4%). These powders were then compacted into discs with 10 mm diameter and 4 mm thickness. Powders were pressed under 254 MPa pressure by using a Hot Press (P/O/WEBER, PO 40 H, Germany). The final sintering was done at 850˚C, 925˚C, 1000˚C and 1150˚C for 2 hour with 1 hour holding time at 600˚C for the elimination of binder. For sintering, heating rate was 5˚C/min and cooling rate was 3˚C/min.

2.2. Characterization

Dielectric properties of the samples were measured by an Impedance analyzer (Wayne Kerr 6500B, UK), for the measurement of dielectric property, both side of the polished pellet was painted by Ag paste. DC resistivity of samples was studied by an Electrometer (6517B Electrometer/High Resistance Meter, Keithley, Germany). Structural properties were investigated by X-ray Diffraction (D8 Advance, BRUKER, Germany) with CuK α (λ = 1.54) radiation and 2 θ ranges from 10˚ to 70˚. Scanning Electron Microscopy (EVO 18 Research: ZEISS, Germany) image of the samples were taken for the analysis of surface morphology.

3. Results and Discussion

3.1. XRD Analysis

Figure 1 shows the XRD pattern of $(Bi_2O_3Fe_2O_3)_{0.4}(Nb_2O_5)_{0.6}$ sintered at different temperature. Two phases were found for samples sintered at lower temperature (850˚C and 925˚C) and the phases are bismuth niobium oxide, $BiNbO_4$ and iron niobium oxide, Fe (NbO_4). Both of the phases has Orthorohombic lattice matched with JCPDS card no: 00-016-0295 and 01-084-1981 respectively. When sintering temperature increased, then single phase Bismuth Iron Niobium Oxide was found. When sample were sintered at 1000˚C then $Bi_{1.34}Fe_{0.66}Nb_{1.34}O_{6.35}$ is found. On the other hand $Bi_{1.721}\delta_{0.089}Fe_{1.056}Nb_{1.134}O_7$ is found for sample which sintered at 1150˚C. Both $Bi_{1.34}$

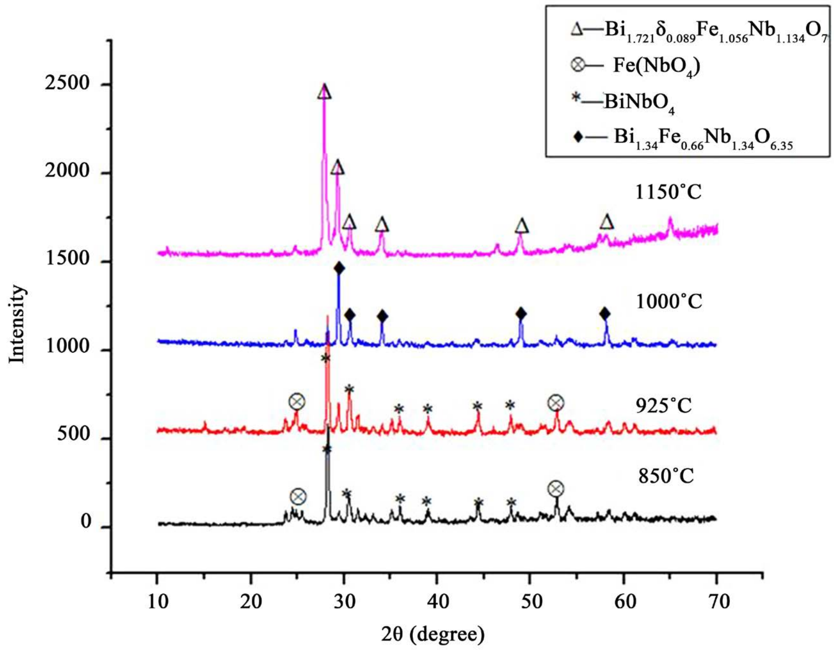


Figure 1. XRD pattern of Nb doped BFO at different sintering temperature.

$Fe_{0.66}Nb_{1.34}O_{6.35}$ and $Bi_{1.721}\delta_{0.089}Fe_{1.056}Nb_{1.134}O_7$ are very similar. One has consecutive peak at 57.451˚ and 58.192˚ but the other has only one peak at 58.256˚. For $Bi_{1.721}\delta_{0.089}Fe_{1.056}Nb_{1.134}O_7$ JCPDS card no is 00-060-0267 and for $Bi_{1.34}Fe_{0.66}Nb_{1.34}O_{6.35}$ JCPDS card no is 00-052-1774.

3.2. SEM

SEM image in **Figure 2(ii)** reveals that grain sizes of the samples are almost identical at comparatively low sintering temperature (850˚C and 925˚C). When temperature increases to 1000˚C then grain size slightly increases and average grain size becomes 1.173 μm. It is clear from the microscopic view that at 1150˚C sintering temperature grain size is the largest among the four samples and the average grain size of **Figure 2(ii)(d)** is approximately 3.47 μm.

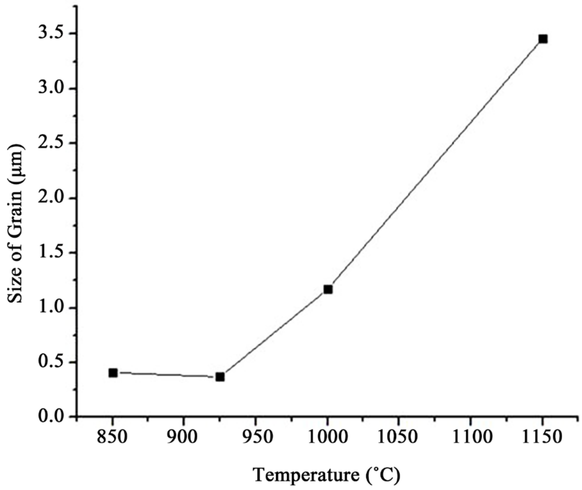
A graphical representation of the grain size with respect to temperature is shown at **Figure 2(i)**. From **Figure 2(i)**, it is observed that up to 925˚C, grain size decreases slightly. This little decrease might be happened according to *Chin-Feng Chung et al.* [5]. But after 925˚C a sharp increase of grain size is found. Rate of grain growth with temperature is higher for higher sintering temperature (1150˚C). Therefore, it can be said that after 925˚C contraction effect was eliminated but grain growth was occurred due to rise of temperature.

3.3. Dielectric Property

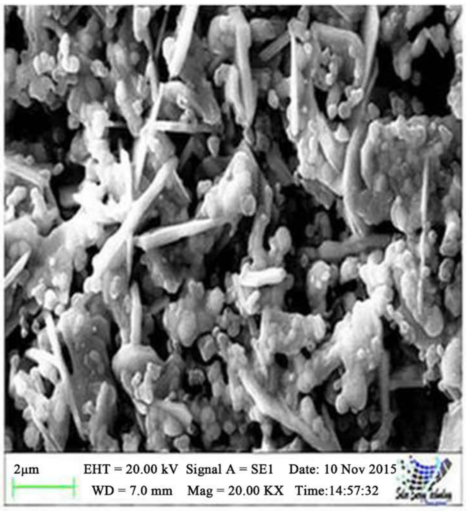
Figure 3 and **Figure 4** represent the variation of dielectric constant and dielectric loss on frequency respectively. It is observed from the **Figure 3**, that the dielectric constant decreases with the increase of frequency. At low frequency higher value of dielectric constant is obtained on the other hand at higher frequency dielectric constant is more or less constant for all samples. This decrease of dielectric constant with the increase of frequency can be happened due to dipole relaxation phenomenon, where the dipoles can follow the frequency of the applied field at low frequencies [6].

From **Figure 4** it is found that dielectric loss decreases with the increase of frequency for the sample sintered at 850˚C, 925˚C and 1000˚C. But for the sample which sintered at 1150˚C shows a Debye like peak at higher frequency. According to Wang *et al*. [7] this higher frequency relaxation is attributed to the ionic relaxation and this type of behavior is supported by Feridoon *et al.* [8].

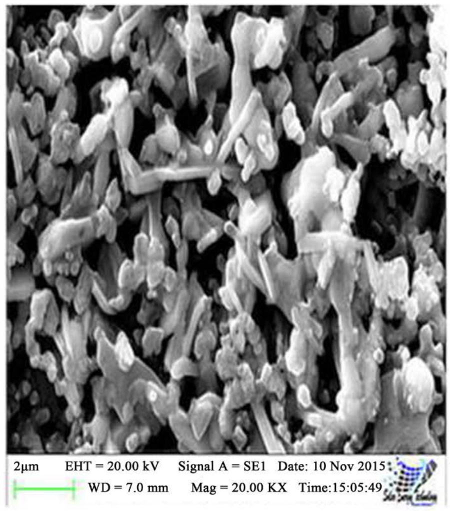
Figure 5 and **Figure 6** represent the effect of temperature on dielectric constant and loss tangent. The dielectric constant and loss tangent remain more or less constant up to 700˚C and only dielectric constant increases



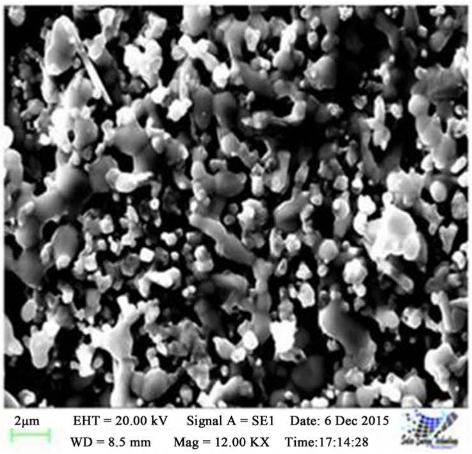
(i)



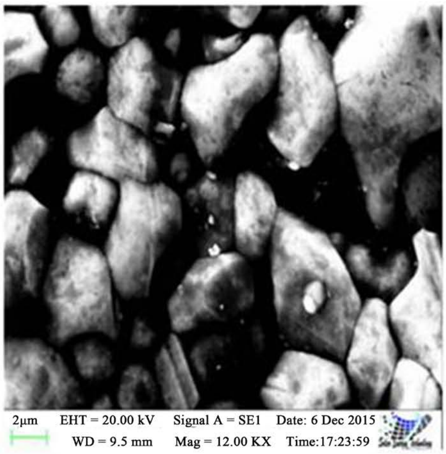
(a)



(b)



(c)



(d)

(ii)

Figure 2. (i) Variation of grain size with sintering temperature. (ii) SEM view of $(Bi_2O_3Fe_2O_3)_{0.4}(Nb_2O_5)_{0.6}$: (a) 850˚C,(b) 925˚C, (c) 1000˚C, (d) 1150˚C.

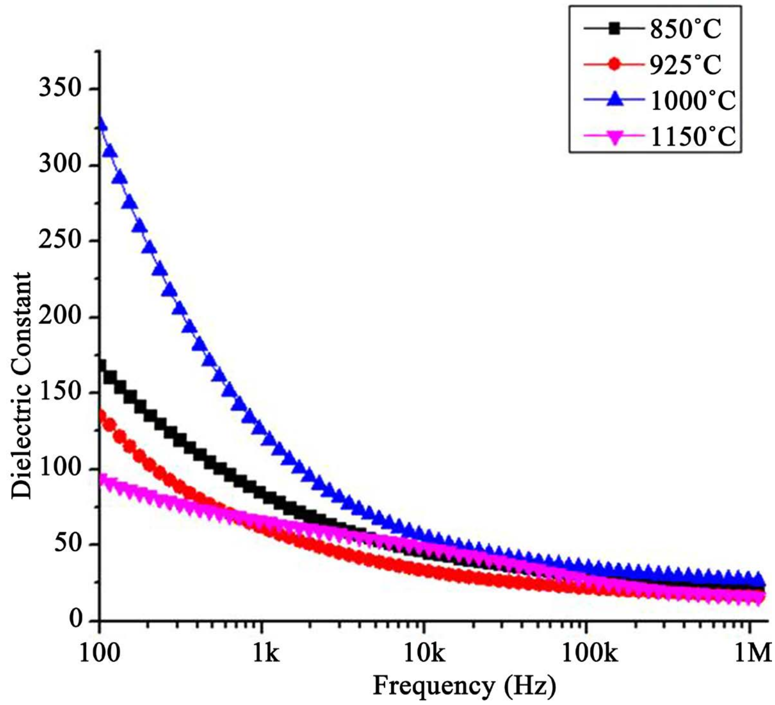


Figure 3. Variation of dielectric loss with respect frequency for $(Bi_2O_3Fe_2O_3)_{0.4}(Nb_2O_5)_{0.6}$.

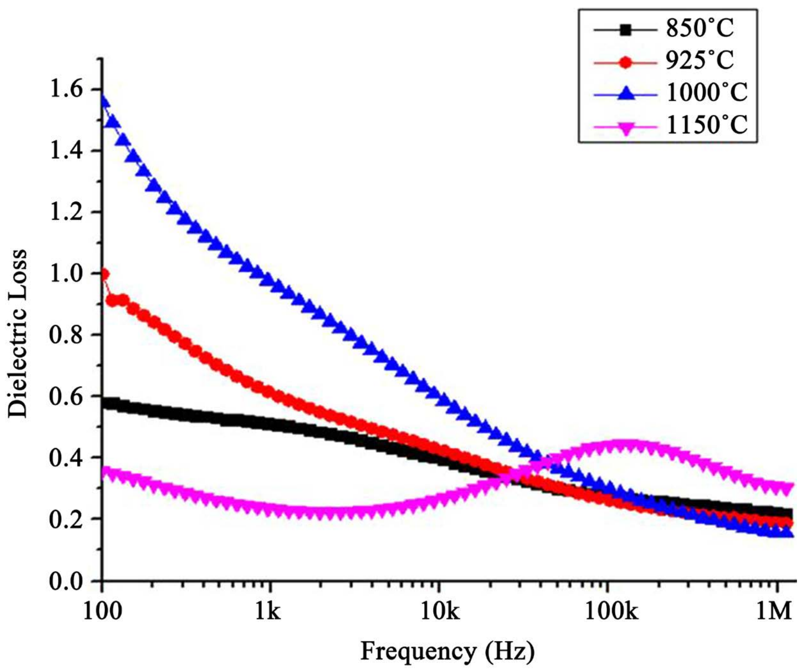


Figure 4. Variation of dielectric loss with respect frequency for $(Bi_2O_3Fe_2O_3)_{0.4}(Nb_2O_5)_{0.6}$.

slightly after 700˚C for the samples sintered at 850˚C and 925˚C, but loss remain constant for the whole range *i.e.*; up to 800˚C. For samples sintered at 1000˚C dielectric constant remain constant up to 800˚C but dielectric loss increases nearly at 800˚C.

But for samples having high sintering temperature (1150˚C) displays a sharp rise of dielectric constant when

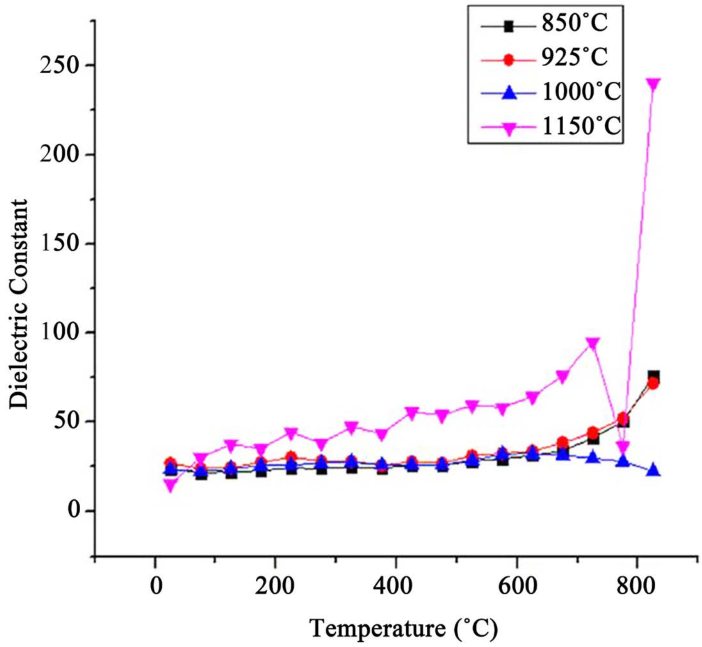


Figure 5. Temperature dependence of dielectric constant for $(Bi_2O_3 Fe_2 O_3)_{0.4}$ $(Nb_2O_5)_{0.6}$.

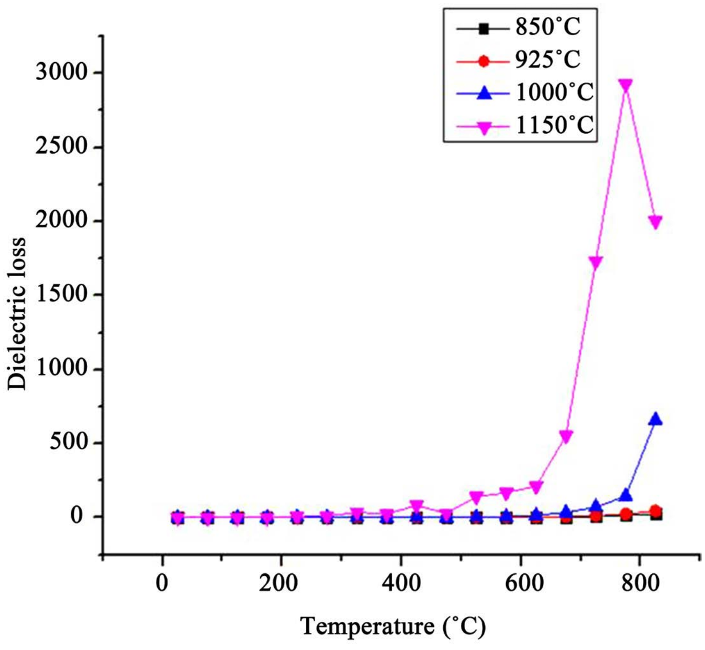


Figure 6. Effect of temperature on dielectric loss for $(Bi_2O_3Fe_2O_3)_{0.4}(Nb_2O_5)_{0.6}$.

measuring temperature is 800˚C. This rise of dielectric constant reveals that an anti-ferromagnetism to paramagnetism transition [9] has occurred. So, it can be said that for this sample Neel temperature (T_N) will be nearly at 800˚C. For other samples this temperature might be found when measuring temperature will be greater than 800˚C because before 800˚C no transition phase occurred for those samples.

3.4. DC Electrical Properties

Figures 7-10 are showing the effect of temperature on resistivity for $(Bi_2O_3Fe_2O_3)_{0.4}(Nb_2O_5)_{0.6}$ at different

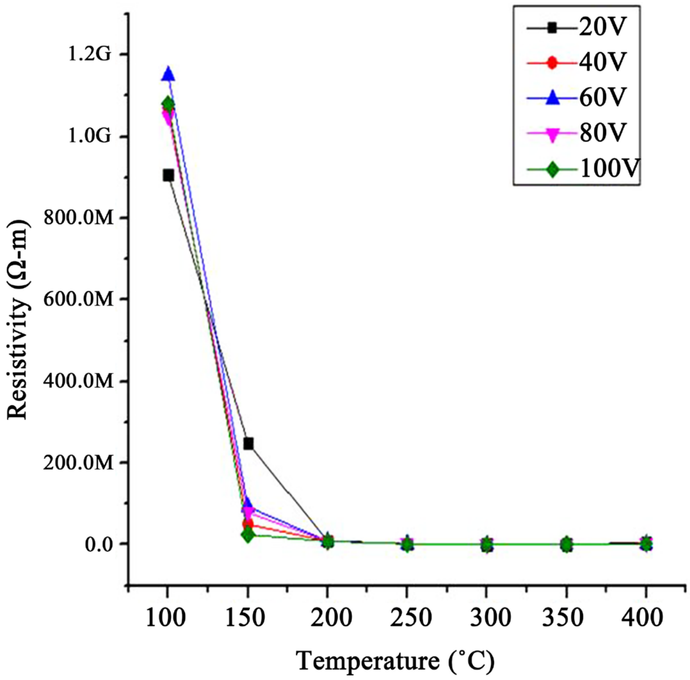


Figure 7. Effect of temperature (T) on DC resistivity for $(Bi_2O_3Fe_2O_3)_{0.4}(Nb_2O_5)_{0.6}$ at 850˚C.

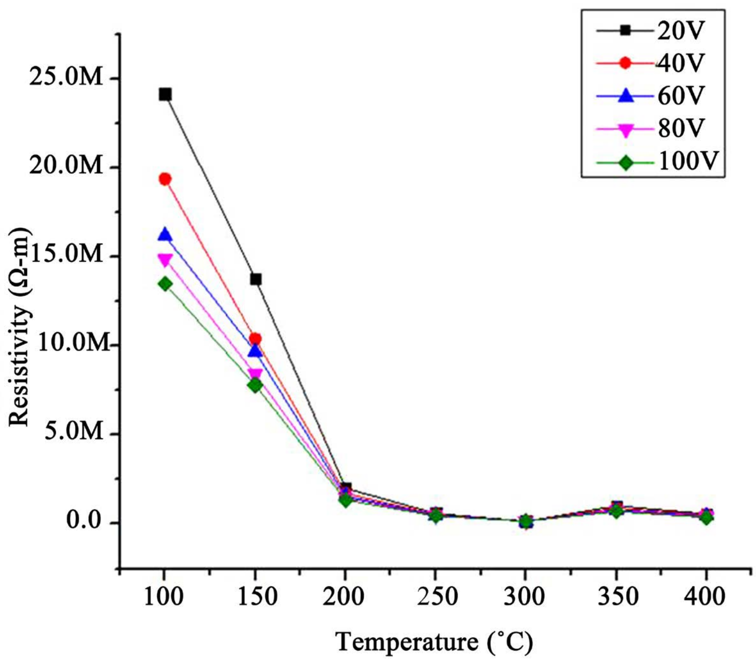


Figure 8. Effect temperature on DC resistivity for $(Bi_2O_3Fe_2O_3)_{0.4}(Nb_2O_5)_{0.6}$ at 925˚C.

voltage. **Figure 7** reveals that for the samples sintered at 850˚C, resistivity of the samples decreases up to 150˚C measuring temperature. When measuring temperature is greater than 150˚C, then resistivity remains more or less constant. Resistivity decreases with the increase of temperature due to semiconducting nature [10]. Therefore it can be said that up to 150˚C, samples sintered at 850˚C showed semiconducting behavior. Samples sintered at 925˚C (**Figure 8**) evolve that resistivity (R) decreases sharply for all voltages up to 200˚C and above 200˚C, it

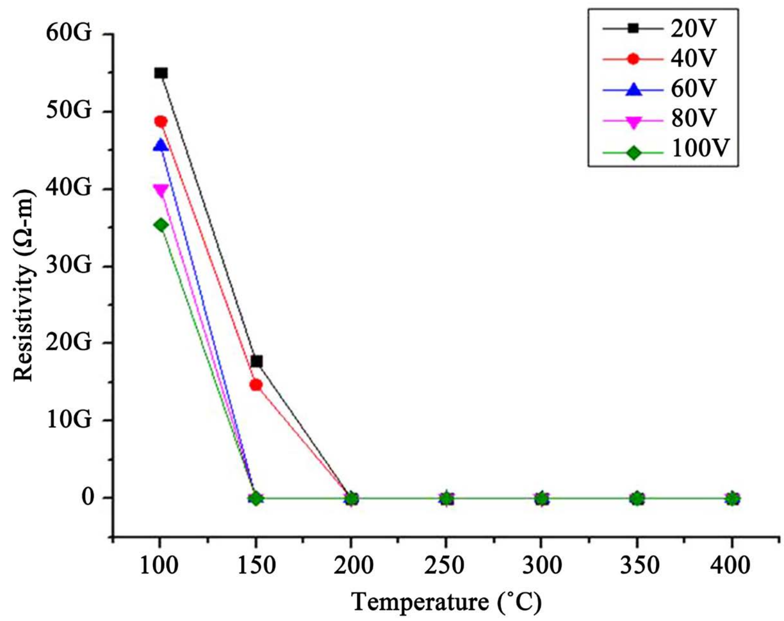


Figure 9. Effect of temperature on DC resistivity for $(Bi_2O_3Fe_2O_3)_{0.4}(Nb_2O_5)_{0.6}$ at 1000˚C.

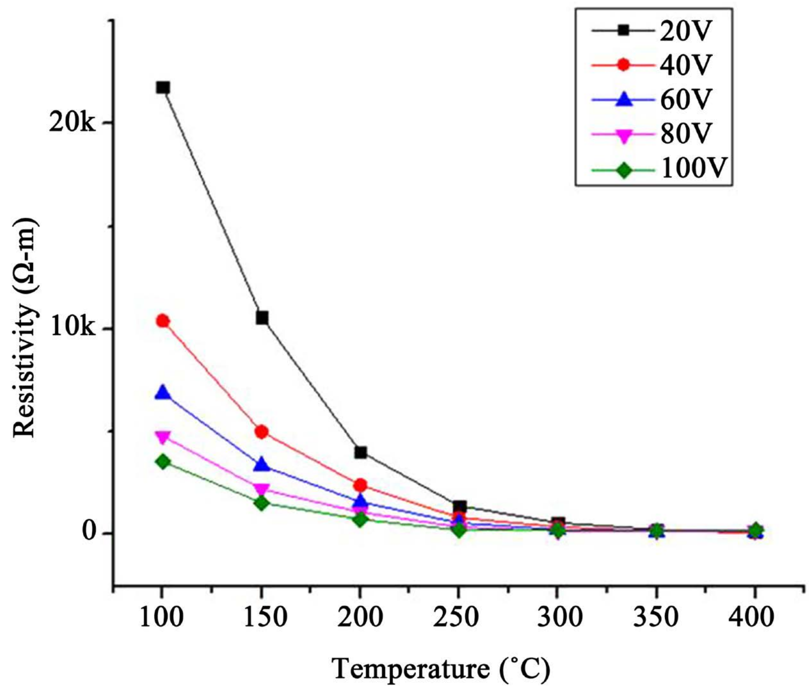


Figure 10. Effect of temperature on DC resistivity for $(Bi_2O_3Fe_2O_3)_{0.4}(Nb_2O_5)_{0.6}$ at 1150˚C.

remains constant. It is also revealed that dR/dT is higher at lower voltage.

As a result, it can be said that specimens sintered at 925˚C show semiconducting nature up to 200˚C. Sample sintered at 1000˚C shows identical response with the samples sintered at 925˚C. Only difference between them is that resistivity falls after 150˚C when comparatively (80 V and 100 V) higher voltage applied.

On the other hand, sample sintered at 1150˚C evolves that resistivity decreases slowly up to 300˚C for all voltages. It is also found that dR/dT of the sample is lower in comparison with other samples.

4. Conclusion

In this research paper effect of sintering temperature on various properties of Nb-doped BFO has effectively performed. It is seen that at higher sintering temperature and a single phase Bismuth Iron Niobium Oxide ($Bi_{1.721}$ $\delta_{0.089}$ $Fe_{1.0956}$ $Nb_{1.134}$ O_7) is obtained. SEM analysis revealed that when sintering temperature increased then grain size also increased causing low resistivity. We get maximum dielectric constant for sample with 1000˚C sintering temperature but further increase of sintering temperature decreased dielectric constant. At last, we have seen that Nb-doped BFO shows semiconducting behavior which is confirmed by D.C. electrical property analysis.

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